PROJECT NUMBER: 2500
PROJECT TITLE: Fundamental Chemistry
PROJECT LEADER: J. I. Seeman
PERIOD COVERED: July, 1987

I. FLAVOR/ODOR CHEMISTRY (Palen, Payne, Secor, Seeman)

A. Objective: To develop new technologies for smoke deliveries of desired flavorants; to prepare new substances for flavor/odor evaluation; to develop methodologies for the analysis of subjective data; to derive relationships between physicochemical parameters and subjectives.

B. Results and Plans: We are in the process of preparing trimethylpyrazine 1 release agents. This chemistry is complicated by the fact that any procedure developed to date in related systems involves the condensation reaction of either a ketone (e.g., p-methoxyacetophenone) or an aldehyde (e.g., p-anisaldehyde 2) with the α-C of an appropriate pyrazine. For 1, there are three such activated positions. We are currently examining purified materials prepared from 1 and benzaldehyde and the total, crude reaction product prepared from 1 and 2. Additional quantities of a tetramethylpyrazine:2,3-butanedione flavor release agent is being prepared. For mechanistic studies on the mechanism of pyrolysis of these compounds, two release agents of 2,6-di-t-butyl-4-methylpyridine (with benzaldehyde and acetophenone) were prepared.

Previously purified D-isomenthone was found to be undecomposed after 3 months at -20°C. It was reduced to d-neoisomenthol in high yield and purity. Additional studies have now demonstrated that all four diasteriomers of menthol crystallize well and can be purified as their terephthalates or 2,6-naphthalenedicarboxylates.

The structures of ca. 700 compounds that comprise the PM odor profiling study are now completely entered into the MACCS database. Corrections and added structures have been directly entered to the database. Names that were in error and typos have also been corrected. The chemical descriptors used in the Boelens odor database analyses have been converted into query language. Substructure will be conducted by a system of layered command programs. A series of fortran programs and command tiles have been prepared for the automated structure-odor search procedures. This sequence will be tested and evaluated in the coming month.

II. TOOL DEVELOPMENT IN MOLECULAR MODELING (Kao)

A. Objective: Develop the necessary algorithms and software to study physical properties of flavor and tobacco related molecules.

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B. **Results**: Efforts continue extending the MOMM approach to TSNA's. Nitrogen-containing compounds are the initial target for this study. It is found that reexamination of the azoalkanes is a prerequisite to provide a consistent, universal, and unique force field for nitrogen-containing molecules. An improved force field is now completed for azoalkanes. New ab initio calculations have been performed to confirm and guide reparametrization. Both the structural and energetic results obtained from MOMM are superior to those previously reported. The average heat of formation deviation from experiment was 0.60 kcal/mol for 12 compounds, which represents an improvement of ca. 40% over the previous force field.

C. **Plans**: The complete report of the improved force field for azoalkanes will be released shortly. The preliminary force field of C-nitroso compounds and organic nitrites is now ready to be finalized and extension of the developed MOMM parameters to N-nitrosamines will be carried out in due course. Hopefully, molecular properties (such as heats of formation, molecular structures, conformational energies, etc.) for TSNA's can be accurately predited by this approach. Mechanistic studies of TSNA formation and degradation will be performed later.

III. INFRARED IMAGING (Leister)

A. **Objective**: To provide programming and data analysis support for the infrared imaging program.

B. **Results**: Preliminary studies on image processor were completed. The goal was to locate the problem with 1000°C calibration point of blackbody source. A second study is underway. A FORTRAN program "WTAVE.F" was developed to calculate weighted averages for pixel luminances of calibration.